



Soft X-Ray Spectroscopy as a tool for materials science

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Outline

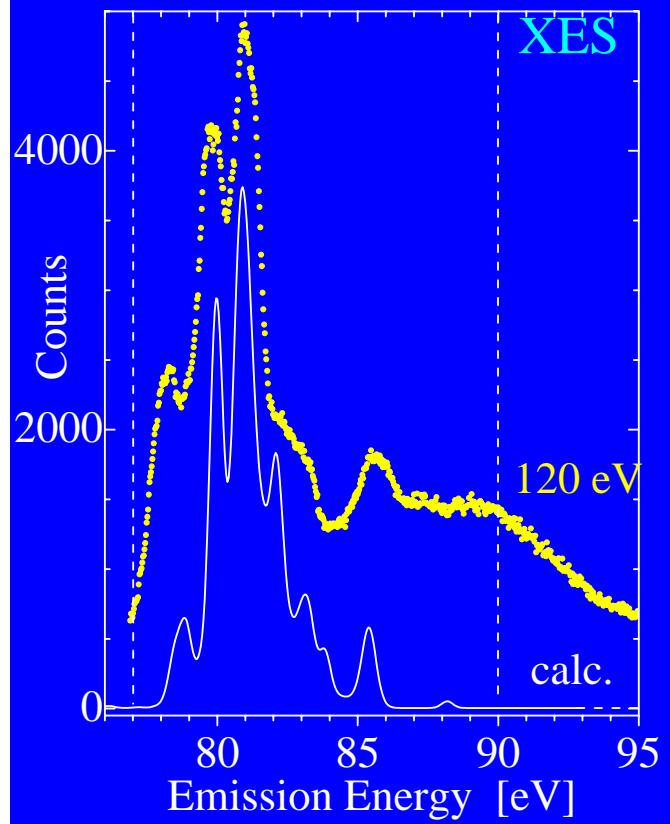
- I. Cascade processes in fluorescence.

➤ II. Study of the electronic structure of $\gamma\text{-Si}_3\text{N}_4$

➤ III. Summary & Acknowledgements

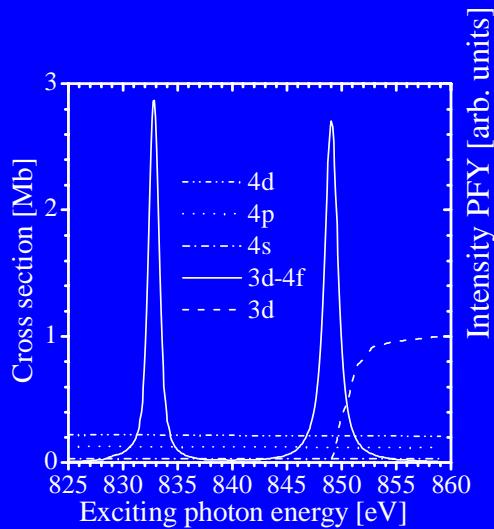
I. Cascade decay in Lanthanum

The question

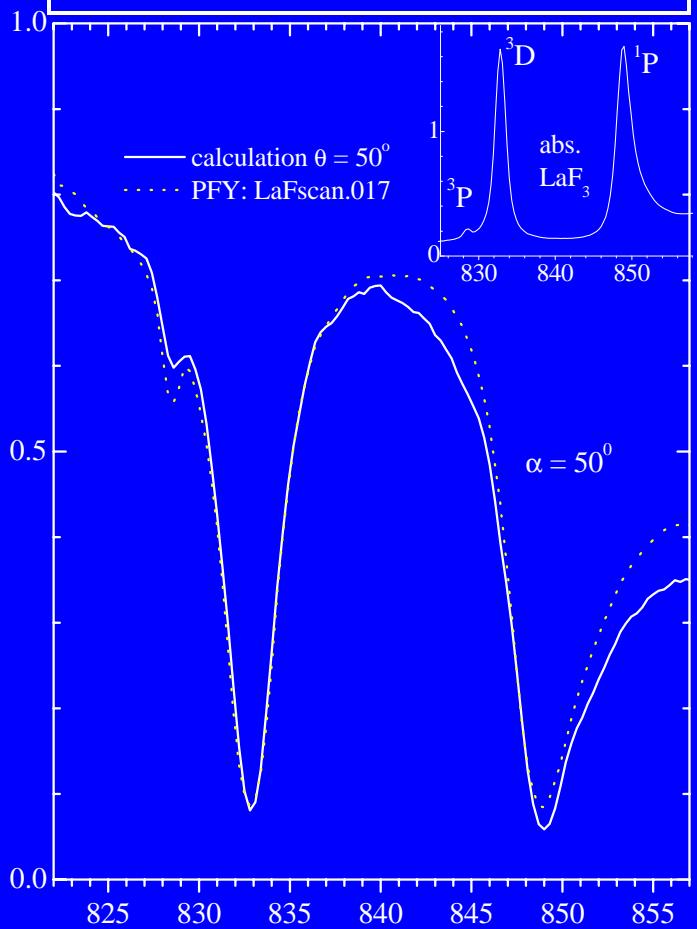


Moewes et al, Europhys. Lett. 62, 582 (2003)

La 5p-4d PFY monitors
number of 4d holes.
Should PFY be constant
760 eV above threshold?



monitoring: F K α PFY (700 eV)
exciting: La 3d-4f (840 eV)

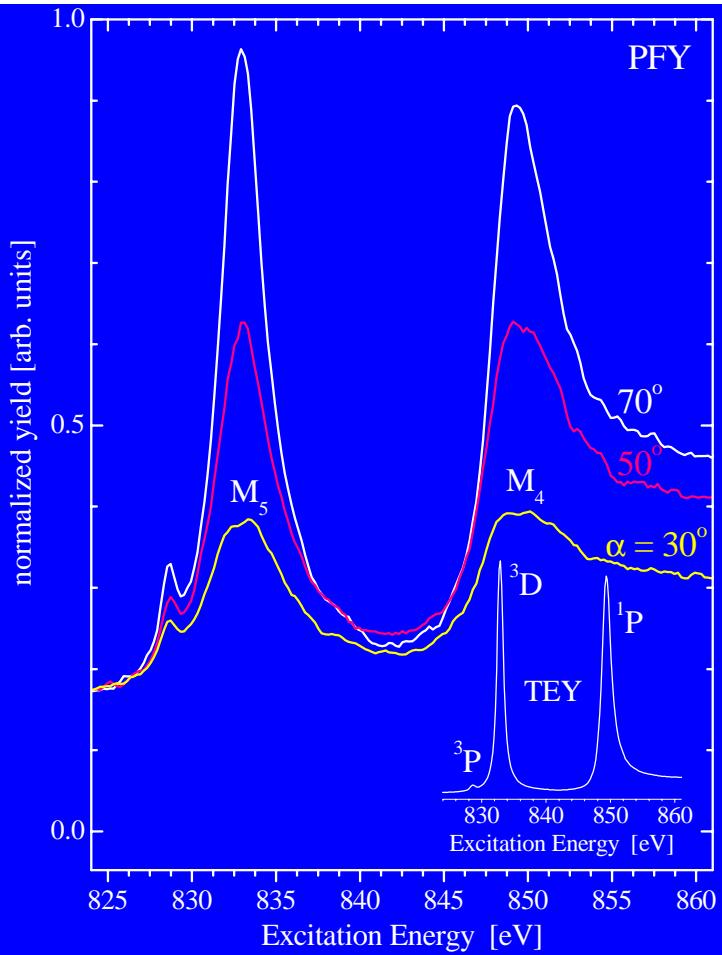


Moewes et al, PRB 62, 15427 (2000)

What happens to (La) emission from a high-lying threshold ($5p \rightarrow 4d$ at 84 eV)
when exciting at lower lying threshold ($3d \rightarrow 4f$ around 840 eV)?

Monitoring another atom

emission: La 5p-4d PFY (84 eV) excitation: La 3d-4f (840 eV)



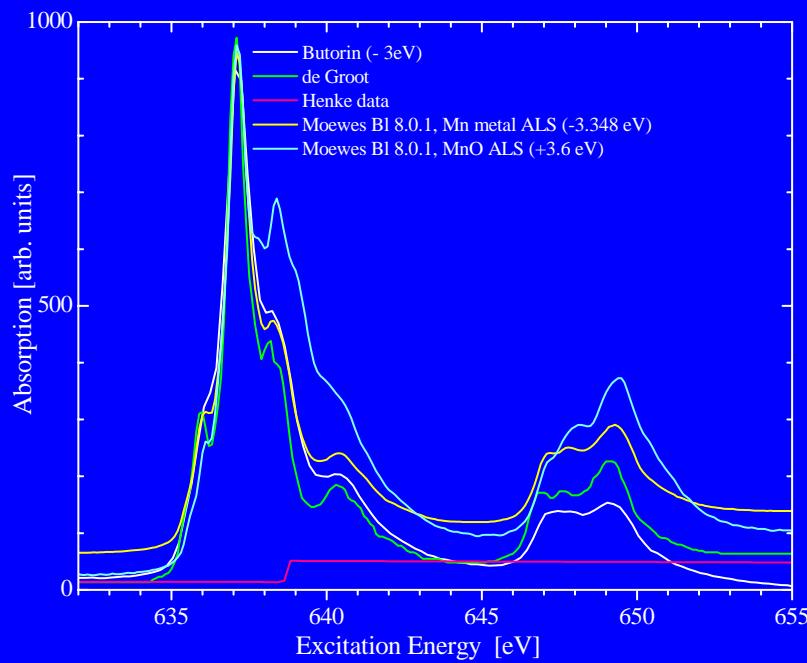
- The 5p-4d partial fluorescence yield is not constant. It shows increase at 3d thresholds and its shape resembles the 3d-4f absorption.
- There is an angular dependence on the angle of incidence.

Model for emitted PFY intensity

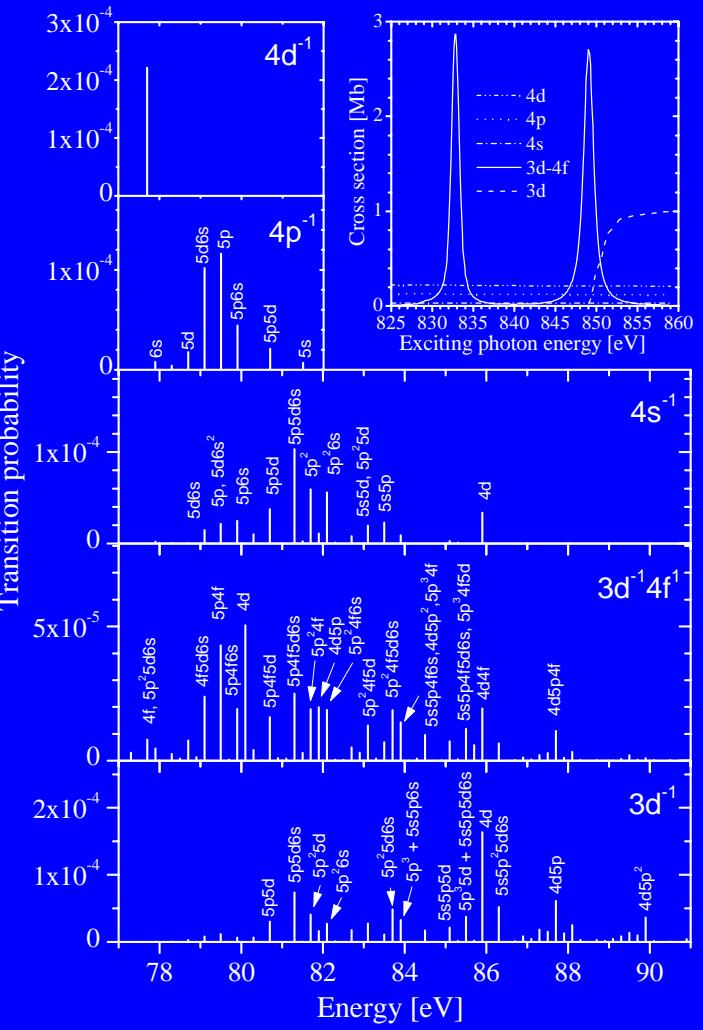
$$\frac{dN_{PFY}}{N_0 d\Omega} \propto \sum_{i,j} \omega_{i,j} \frac{1}{\mu + \mu_{i,j} \cdot \tan \alpha}$$

(2) Correction for self-absorption:

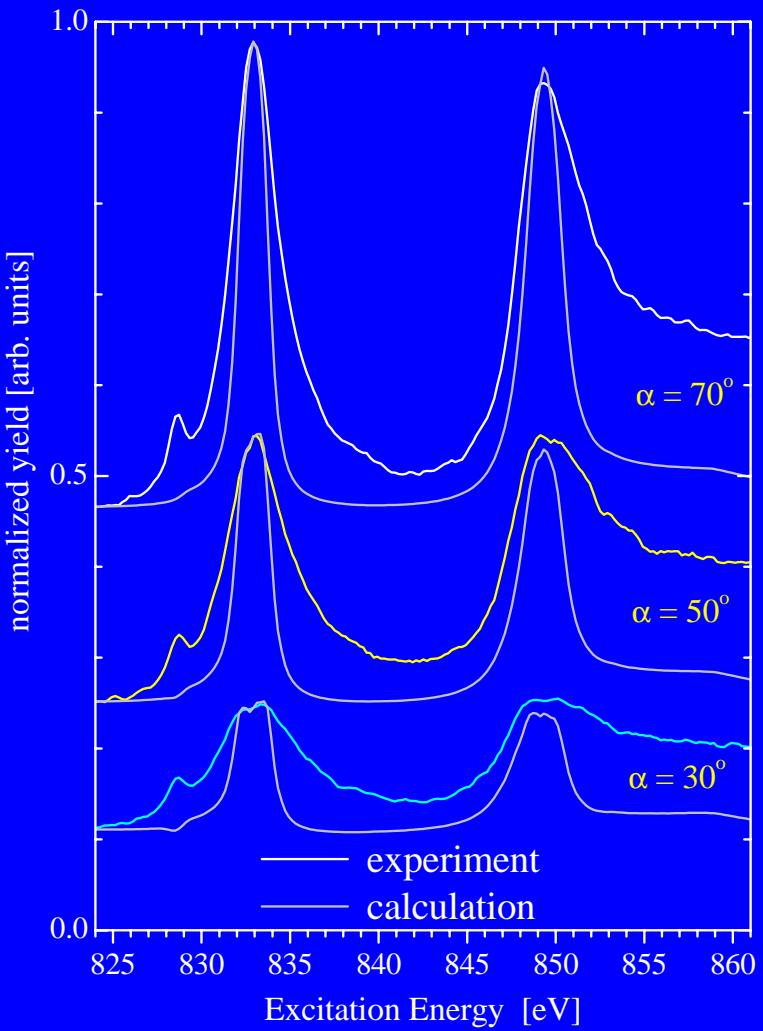
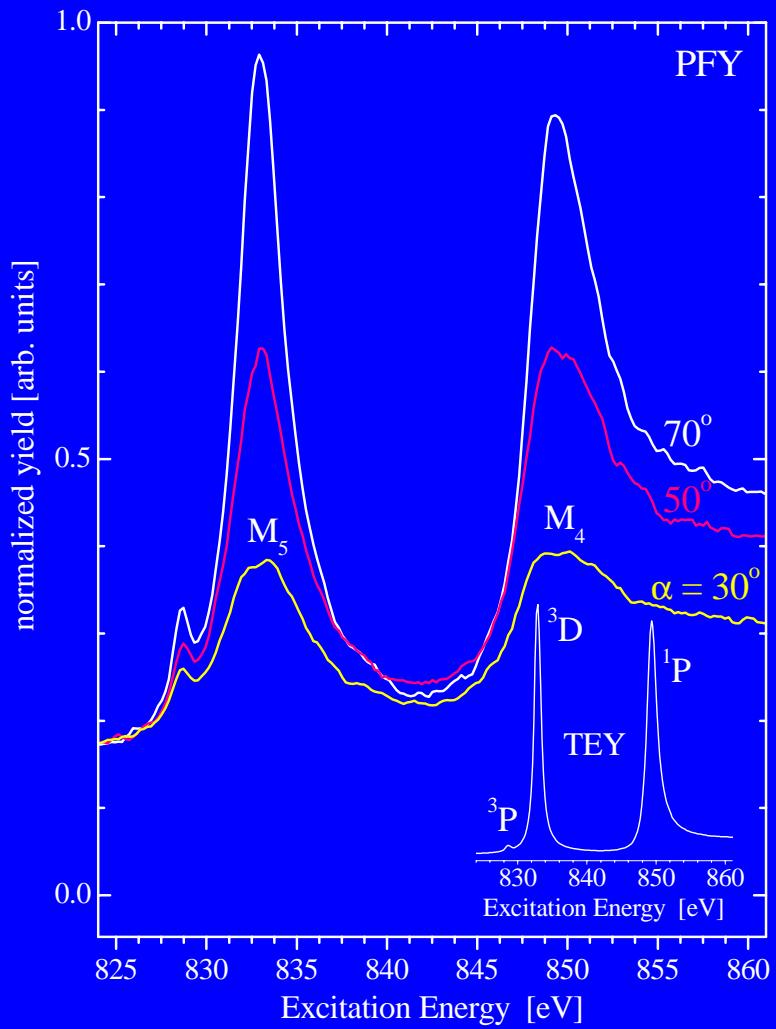
- “careful” measurements of TEY, PFY and
- $\mu / \mu_{i,j}$
- same exp. resolution for XES, XAS



(1) Cascade calculations



Comparison model and experiment



- Cascade processes need to be taken into account.
- Contrast agrees well for calc. and exp. but
- integral exp. intensity is 2.4 times larger than for calculation.

III. Ultrahard new Si phase γ -Si₃N₄

The three phases of Si_3N_4 and $\text{Si}_2\text{N}_2\text{O}$:

Original Spinel (mineral): MgAl_2O_4

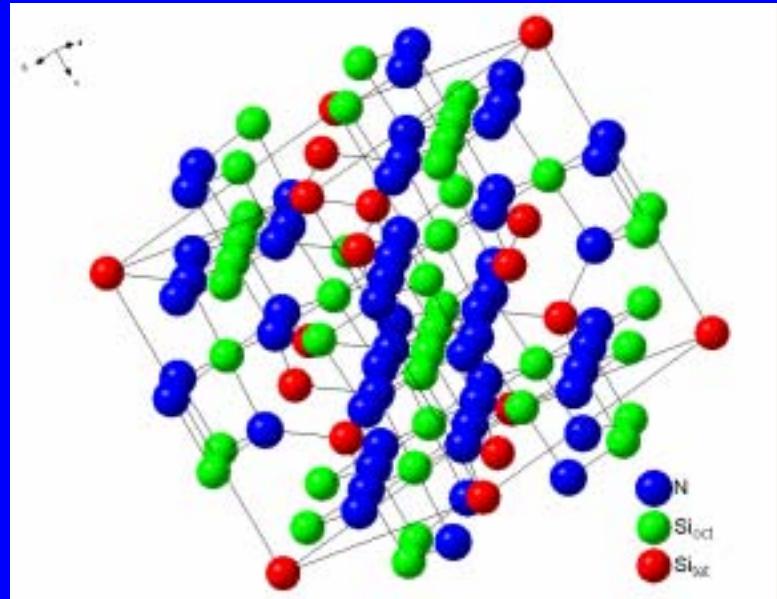
Four forms of Si_3N_4 observed:

$\alpha\text{-Si}_3\text{N}_4$

$\beta\text{-Si}_3\text{N}_4$

$\gamma\text{-Si}_3\text{N}_4$

Amorphous Si_3N_4



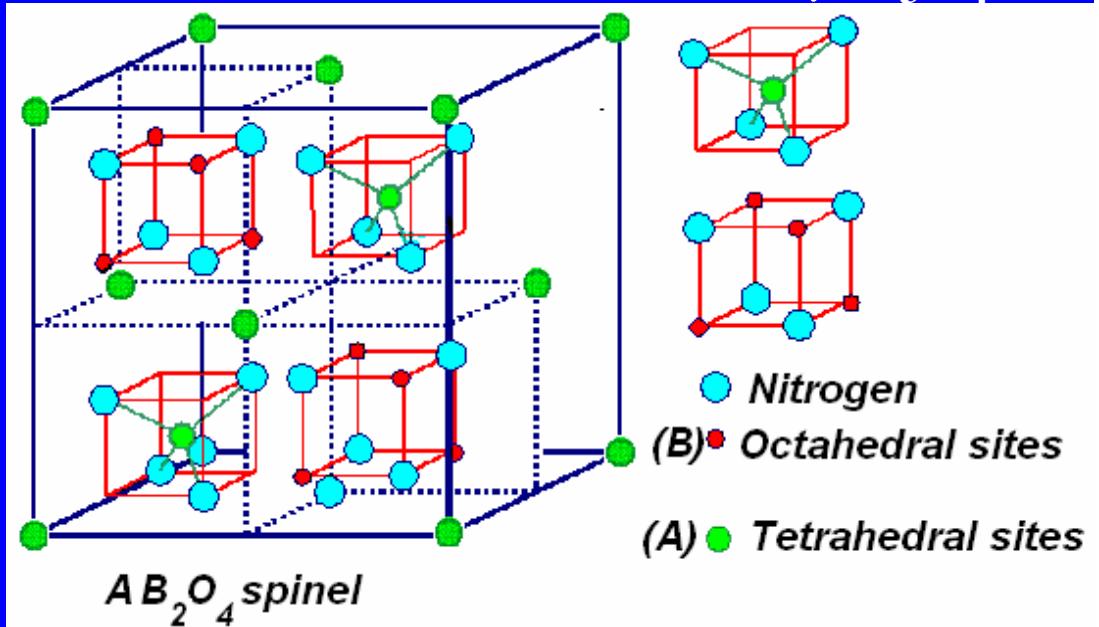
$\text{Si}_2\text{N}_2\text{O}$

Cubic spinel structure $\gamma\text{-Si}_3\text{N}_4$

Three possible locations of Si atom

1 Tetrahedral atom

2 Octahedral atoms



Why spinel Silicon nitride $\gamma\text{-Si}_3\text{N}_4$?

- Newest synthesized phase: at high T (1800 K) and p (13 GPa) [Zerr et al, Nature 400, 340 (1999)].
- Considered 3rd hardest material next to diamond and c-BN.
- Hardness, thermal stability, resistance to oxidation are interesting for applications (LED & other semiconductor devices).
- Theory: large gap semiconductor: 3.45 eV (direct) UV [Mo et al, PRL 83, 5046 (1999)] .
- Theory: tunable gap when doped with Al, O [Oba et al, APL 78, 1577 (2001)].

Our Questions:

What is the band-gap?

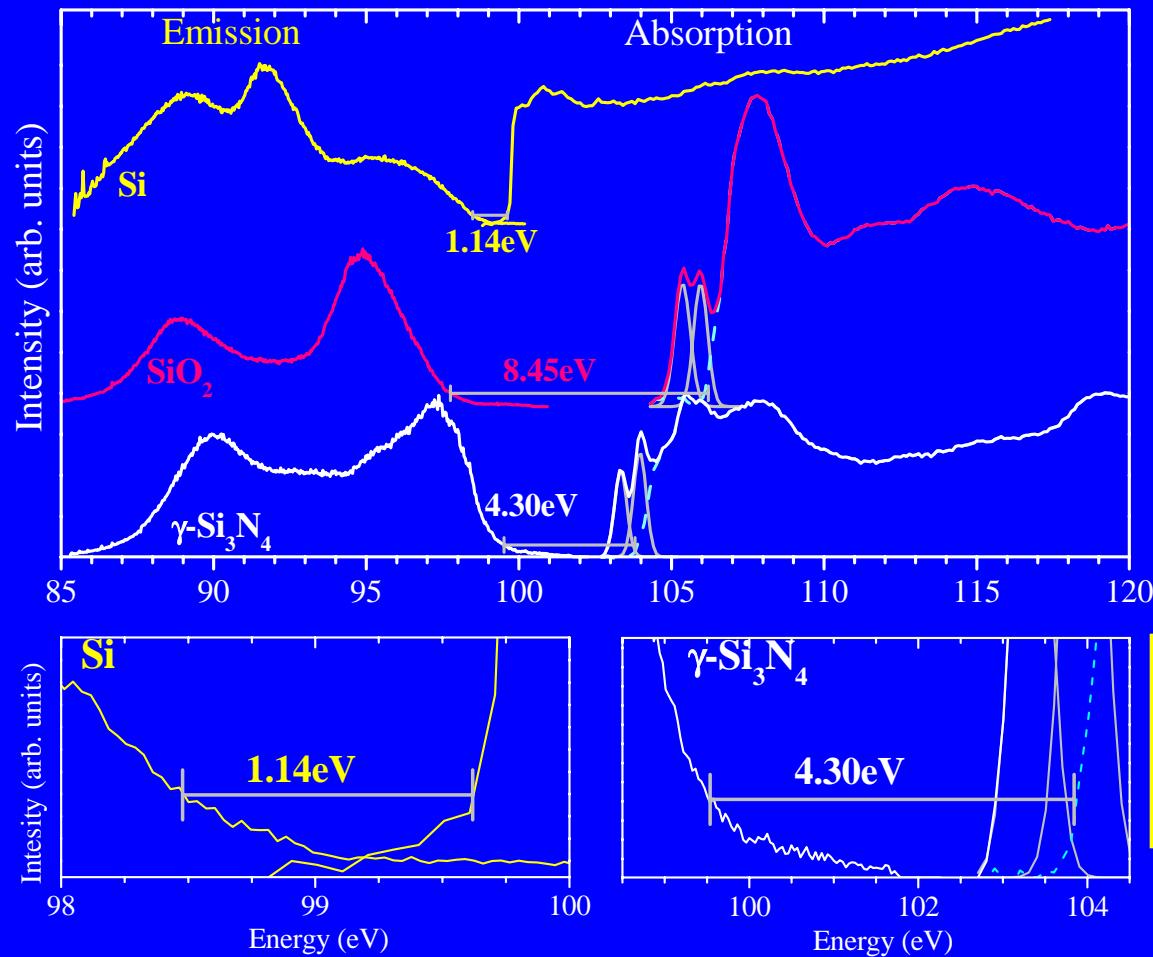
How different are tetrahedrally and octahedrally coordinated Si?

Can we spectroscopically distinguish the non-equivalent Si sites?

The band gap of $\gamma\text{-Si}_3\text{N}_4$

Problem: No single crystal available, band gap measurements are difficult.

Solution: Measure occupied (XES) and unoccupied (XAS) density of states:



S. Leitch et al., J. Phys.:
Cond. Mat. 16, 6469 (2004)

Without accounting for
“exciton”, the band gap
value would be 3.42 eV.

Our experimental determination of band gap for $\gamma\text{-Si}_3\text{N}_4$: 4.3 ± 0.25 eV

Theory: 3.45 eV [Mo PRL 83, 5046 (1999), own calc. (Ching)].

Other Exp. value (UV abs.) : 3.3 eV [Zerr et al, Act. Crystallogr. 58, C47 (2002)].

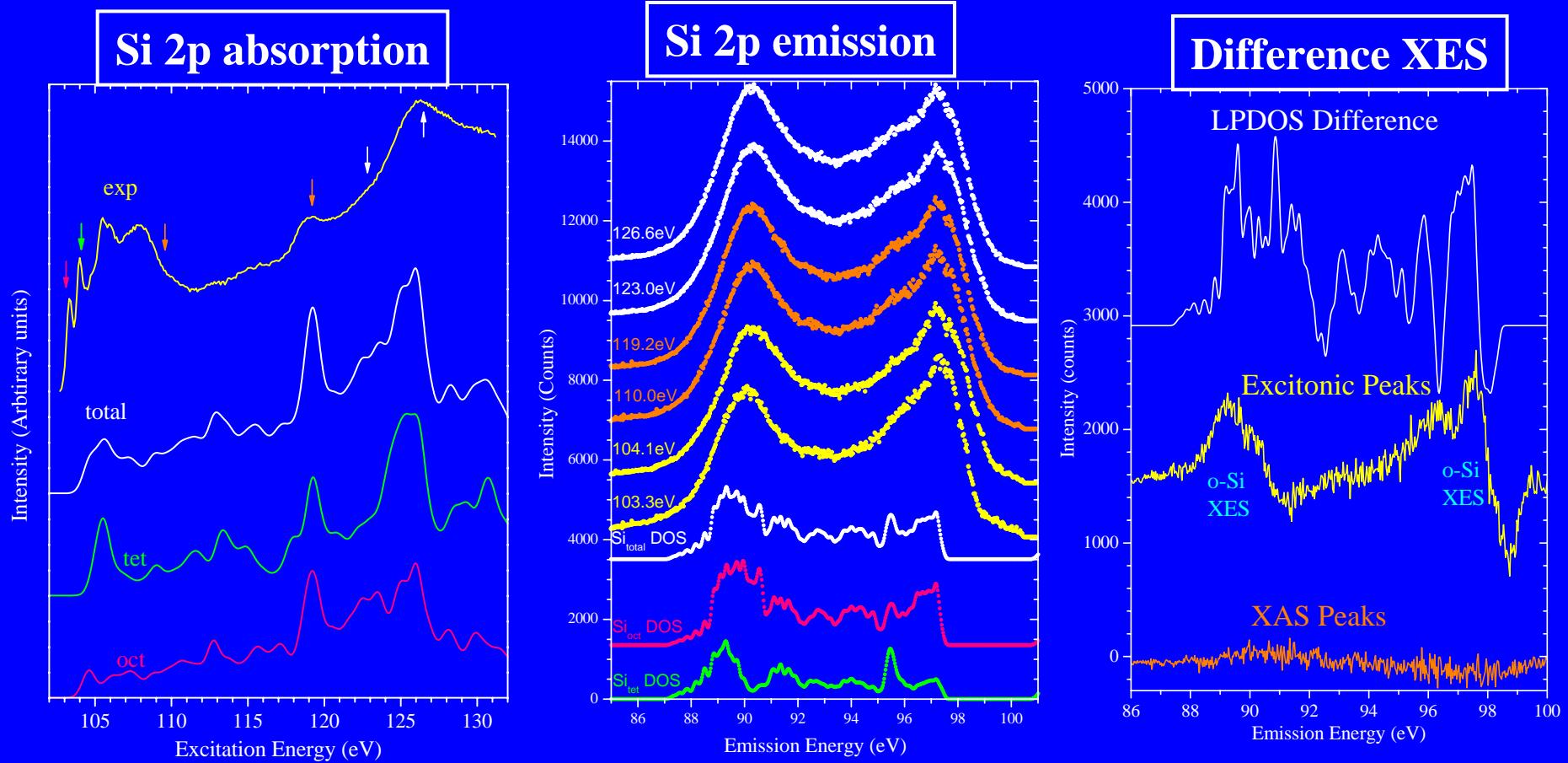
Problems concerning band gap of $\gamma\text{-Si}_3\text{N}_4$

The following things have to be considered:

- XAS Spectra are affected by presence of core hole (not as much as XES!)
→ shifts XAS to lower energy by 0.5 eV : decrease of band gap.
- Si spin-orbital splitting of 0.6 eV
→ produces two (identical) XES, which leads to reduction of gap by 0.5 eV.
- Quantum confinement due to size of particle [vanBuuren, PRL 80 (1998)]
→ widens gap 0.26 eV (VB 0.2 eV, CB +0.06 eV) for 3.2 nm particles
but for our 10 – 50 nm particles effect is much smaller than 0.2 eV.
- Phonon effects: cause spectral broadening – for polar materials
→ effect in ionic SiO_2 but not covalently bonded Si_3N_4 .

However, our band-gap determination uses reference samples (Si , SiO_2).

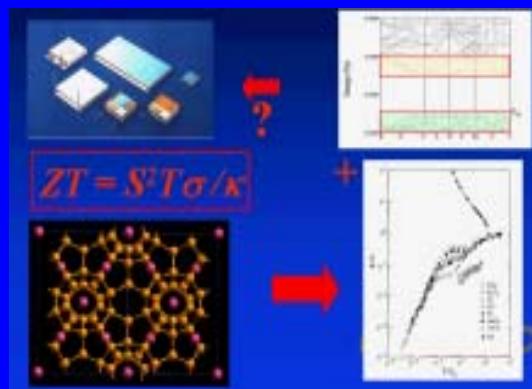
Exciting non-equivalent sites of $\gamma\text{-Si}_3\text{N}_4$



- Si L2,3 emission spectra look very similar.
- Use difference spectra to visualize diff. between spectra (oct. – tet.).
- Only when exciting on excitonic states, we spectroscopically can distinguish the non-equivalent Si sites.

Electronic structure of Clathrates

- M_8Si_{46} with $M=Na, K$
- Calc. show band gap 1.9 eV for Si_{46} (1.14 eV for Si)
⇒ promising candidate for optoelectronic devices!
- Clathrates can form nano sized clusters and have promising thermoelectric properties.



Collab.:
J.S. Tse, NRC

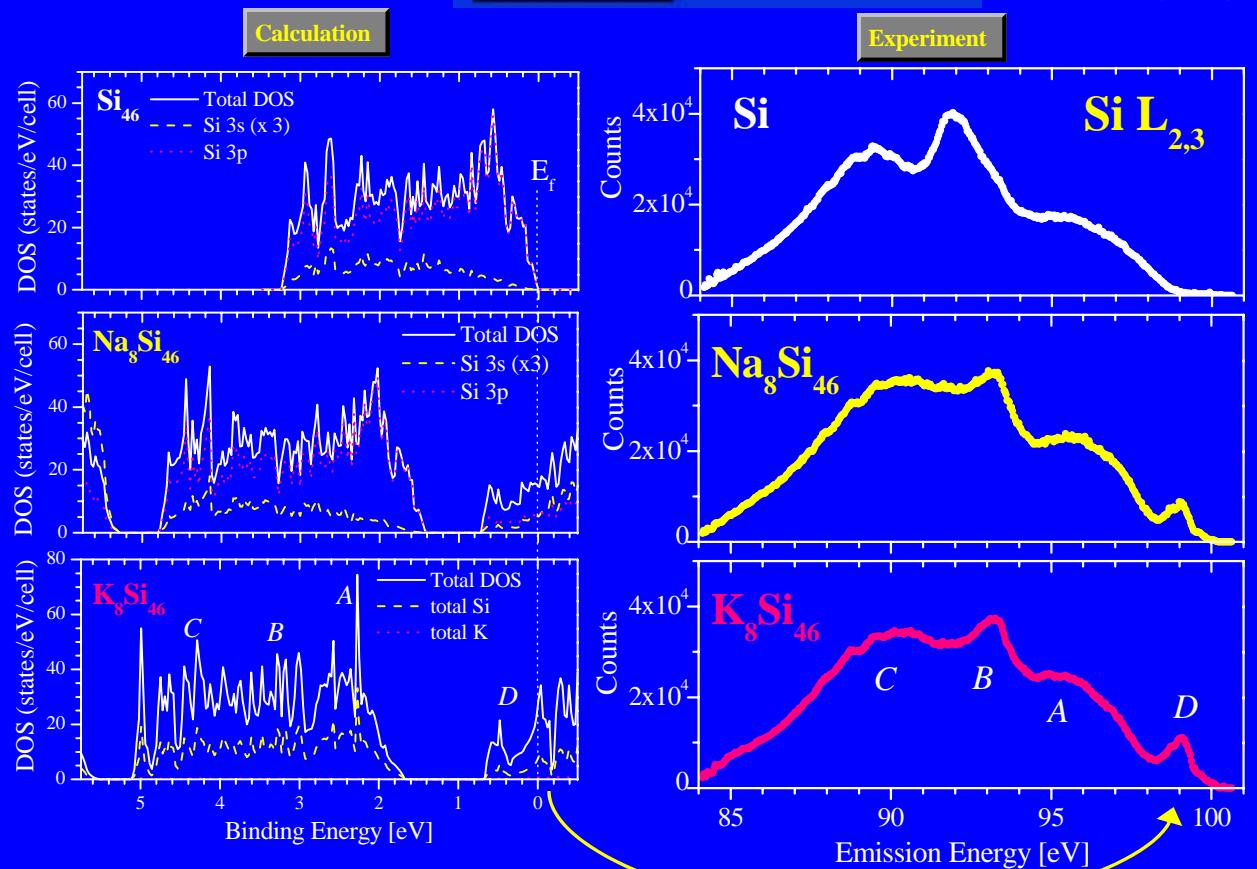
Moewes, Tse
Phys. Rev. B 65,
1531061 (2002)

Questions:

- Interaction metal impurity atoms and Si frame?
- Recent models indicate metal guest neutral?

Study $Si L_{2,3}$ emission:

VB (3d) \rightarrow 2p_{1/2,3/2}



Conclusions:

- ⇒ Complete charge transfer from Na/K to Si.
- ⇒ Rigid band approximation is appropriate one.

Additional Na/K electrons fill conduction band and give rise to feature D.

III. Acknowledgements

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